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Issued February 28, 1912.

United States Department of Agriculture,

BUREAU OF CHEMISTRY—Circular No. 85.

H. W. WILEY, Chief of Bureau.

A MODIFICATION OF THE HERZFELD-BOHME METHOD FOR THE DETECTION OF MINERAL OIL IN OTHER OILS.

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INTRODUCTION.

This modification was devised to detect small additions of mineral oil to turpentine. It is not unusual to add 1' gallon or even less mineral oil to a barrel of turpentine, and the detection of this quantity by the original method is often uncertain. The modification is of course applicable to the detection of mineral oils in other oils and has been applied successfully to neat's-foot, linseed, lard, and cotton-seed oils and to coal-tar creosote.

In 1906 a comparative study of turpentine obtained from various sources and with different processes was begun in this laboratory. The primary purpose of this work was the determination of the extent and quantity of adulteration with inferior oils, the most common adulterants, it was found previously, being some of the petroleum products. The previous experience of the laboratory, together with the data found in the literature, led to the conclusion that the method devised by Herzfeld-Bohme¹ promised to give the most definite results as well as to be the simplest and most rapid in execution.

The first experience with the method developed the fact that it gave erratic results on the same turpentines when different lots of the acid, prepared in accordance with the directions, were used. This, Donk found, was caused by the difference in concentration of the different lots of acid, due to irregularities in concentration of different consignments of ordinary, and of fuming, acid. The amount of

¹ Chem. Ztg., 1906, 30: 631.

residue from pure turpentines was found to vary between 1 and 5 per cent; the refractive index of this residue was often so near that of turpentine that the detection of small percentages of mineral oil was rendered uncertain. Donk suggested the use of acid of definite concentration and conducted experiments for the purpose of determining what concentration was most suitable.

Study of the old method showed other sources of error and uncertainty. The errors in reading volume, when a burette or graduated tube is used, are large. The use of a Babcoëk milk bottle as the reaction flask eliminated this source of error. The temperature of the reaction and the thoroughness with which the acid and turpentine are mixed were also found to be factors influencing the results materially. Finally, the method as commonly stated permits a residue of 10 per cent on a pure turpentine and this quantity is often greater than the amount of mineral oil present. Some latitude must be allowed in the results obtained, even with the modified method. Absolute harmony between the volumes, refractive indices, and consistencies of the residues, even on the same turpentine with the same acid, is not to be expected. This is probably due to the complicated reaction (which does not always proceed in the same way) taking place between the acid and the turpentine. The extent of the reaction is controlled very largely, as has been stated, by the thoroughness with which the acid and turpentine are mixed. As this mixing unavoidably differs somewhat, with each sample, a certain latitude in results must be allowed.

The procedure employed in working out the details of the modified method was as follows: To 20 to 25 cc of acid in a Babcock milk bottle (cooled in ice water to prevent violent action) add slowly 5 cc of turpentine; again cool and gradually mix by shaking, with intermittent cooling, shaking thoroughly toward the last to insure intimate contact of the residual turpentine and acid, the total time for adding the turpentine and thoroughly mixing it being about five minutes. Then add concentrated acid to bring the residue into the graduated neck, whirl the flask for a few minutes in a centrifuge or allow it to stand over night, and read the volume of residue.

CONTROL OF THE CONCENTRATION OF THE ACID.

It was found that the concentration of the sulphuric acid must be definitely controlled in order to insure constant results on the same turpentine. To this end it was necessary to prepare the acid by titration, as 37.8 normal acid gave much larger residues by this modification than 38 normal acid. The effect of the concentration of the acid on the volume of the residue is shown in the table following.

TABLE I.—*Effect of concentration of acid on volume of residues.*

No.	Material.	Residue with—		
		36 normal acid.	37 normal acid.	38 normal acid.
		<i>Per cent.</i>	<i>Per cent.</i>	<i>Per cent.</i>
1173	Gum spirits.....	5.2	0.4	0.2
1232	do.....	8.4	1.6	.1
2655	Steam distilled wood turpentine.....	9.6	3.0	.4
1175	Destructively distilled wood turpentine.....	7.2	.8	.2
1176	do.....	10.4	3.2	.4
1229	do.....	9.6	3.2	.2
1182	Heavy oil from steam distilled wood turpentine.....	13.6	8.8	4.8

From these results it will be seen that on such spirits of turpentine, the residue, when 36 normal acid was used, varied from 5 to 10 per cent; when 37 normal acid was used, it varied from 0.4 to 9 per cent; and when 38 normal acid was used, the variation was from 0.2 to 0.4 per cent.

The residues left by the 36 and 37 normal acid are entirely too large to enable one to detect with certainty the presence of small adulterations with mineral oil. Indeed, the residue from the 36 normal acid is larger than is often obtained on adulterated samples and the refractive indices of these residues are too close to those of the ordinary turpentines to be used safely to prove the presence of mineral oil.

EFFECT OF HEAT.

The temperature of the reaction taking place when the turpentine is added to the acid influences greatly the volume of the residue from a turpentine. Twenty-five cc of the ordinary 1:3 acid mixture and 5 cc of turpentine at room temperature left a residue of 7.4 per cent; at 65° C. of 5.6 per cent; and at 95° C. of 1.6 per cent. Twenty-five cc of the acid and 5 cc of ordinary kerosene at room temperature left a residue of 99 per cent; at 65° C., 86 per cent; at 95° C., 84 per cent. Two cc of the kerosene residue from the above experiment when mixed with 25 cc of the 1:3 acid mixture at room temperature left a residue of 95 per cent and at 95° C. a residue of 91 per cent.

It was found, however, that when the temperature was above 65° C. the reaction between the acid and the turpentine was so violent that portions of the mixture were lost or in some instances explosions resulted. For this work, therefore, it has been found necessary to control the temperature. Further, it was also found that high temperatures promoted the loss by volatilization of small quantities of the light oils when these were present and unacted upon by the acid.

RATIO OF ACID TO TURPENTINE.

The volume of the residue was found also to vary with the ratio between the volume of acid and oil used, the larger volume of acid giving in each case the smaller residue.

The results obtained in experiments on this point (using 38 normal acid) are shown in the following table:

TABLE II.—*Effect of ratio of acid to turpentine.*

Substance.	Acid.	Residue.		Refractive index of residue.	Consistency of residue.
		cc	Per cent.		
Gum spirits.....	15	0.09	1.8	1.5138	Viscous.
	25	.02	.4	1.5140	Do.
	50	None.			
2.5 per cent light mineral oil.....	15	.15	3.0	1.5002	Slightly oily.
	25	.05	1.0	1.4965	Do.
	50	.02	.4	1.4760	Do.
5 per cent light mineral oil.....	15	.19	3.8	1.4850	Do.
	25	.12	2.4	1.4750	Clear and limpid.
	50	.08	1.6	1.4675	Do.
10 per cent light mineral oil.....	15	.32	6.4	1.4750	Slightly oily.
	25	.25	5.0	1.4693	Clear and limpid.
	50	.20	4.0	1.4620	Do.

It will be seen from these figures that the percentage of residue from both pure spirits and adulterated spirits fell rapidly when the quantity of acid used was largely increased. With the adulterated spirits containing 2.5 per cent of light mineral oil, the use of 50 cc of acid reduced the residue to the percentage usually obtained from pure spirits of turpentine when 25 cc of acid are used. With 25 cc of acid, the residue from the turpentine adulterated with 2.5 per cent of mineral oil is but 1 per cent; from that adulterated with 5 per cent of mineral oil, it is 2.4 per cent; from turpentine containing 10 per cent of mineral oil, it is 5 per cent, showing that with different quantities of acid or turpentines containing 10 per cent of adulteration or less the recovery of mineral oil as residue is approximately one-half.

When 50 cc of the acid is employed, the recovery is considerably less than one-half. It will be observed, however, that when but 0.4 per cent of residue was left on treating the turpentine adulterated with 2.5 per cent of mineral oil, with 50 cc of acid the refractive index of the residue was 1.476, showing clearly that it is not of the same nature as that obtained by like treatment from pure turpentine.

FURTHER WORK ON CONCENTRATION OF THE ACID.

In order to secure additional data on the effect of the concentration of the acid on mineral oils, a number of so-called turpentine substitutes and adulterants, such as are offered on the market for these purposes, were treated according to the method with 25 cc of acids

of various concentrations. The reactions were conducted at 65° C., and 5 cc of oil were used in each case. The results are given in Table III:

TABLE III.—*Effect of acid of various concentrations on mineral oils.*

L. and P. No.	Substance.	Concentration of acid in terms of the normal.	Residue.	Refractive index at 20° C.	
				Residue.	Original substance.
			<i>Per cent.</i>		
8046	Texene.....	34.6	98.4	1.4420	1.4430
		36.0	96.4	1.4409	
		37.0	93.0	1.4394	
		38.0	70.2	1.4387	
8047	No. 99, special. (Sp. gr. 0.8605).....	34.6	93.0	1.4462	1.4692
		36.0	87.4	1.4639	
		37.0	82.0	1.4610	
		38.0	69.2	1.4590	
8048	No. 18, special. (Sp. gr. 0.8177).....	34.6	93.6	1.4460	1.4478
		36.0	90.4	1.4447	
		37.0	85.8	1.4430	
		38.0	67.8	1.4419	
6547	Terebentine.....	34.6	96.2	1.4438	1.4466
		36.0	88.4	1.4424	
		37.0			
		38.0	68.8	1.4419	
6377	Turpentine substitute.....	34.6	88.4	1.4230	1.4342
		36.0	86.4	1.4270	
		37.0	83.6	1.4260	
		38.0	65.6	1.4234	
6427	NU turps.....	34.6	79.6	1.4421	1.4479
		36.0	78.0	1.4402	
		37.0	74.0	1.4380	
		38.0	65.6	1.4370	
	Kerosene.....	34.6	92.0	1.4395	
		36.0	90.0	1.4375	
		37.0	86.4	1.4348	
		38.0	73.0	1.4328	
	Naphtha.....	34.6	93.6	1.4122	1.4135
		36.0	91.0	1.4115	
		37.0	89.4	1.4099	
		38.0	67.2	1.4065	

Inspection of the table shows that all of these materials, with the exception of kerosene, behave similarly and that with 38 normal acid the residue from each is approximately 68 per cent. The kerosene is acted upon to a slightly less degree, the residue being 73 per cent. It will be observed that the refractive indices of the residues decreased with the increasing concentration of the acid employed and in every case the residues had lower refractive indices than the original oils. This behavior is diametrically opposite to that of turpentine, where the refractive index of the residue is always much higher than that of the original oil.

The refractive index of residues from pure turpentine treated with comparatively weak acid for the time specified in this modification is usually considerably lower than when the turpentine is treated with 38 normal acid. Thus, on one sample, when 38 normal acid was employed the residue was 0.4 per cent; its refractive index was 1.5120. When 1 part of concentrated to 2.5 parts of 38 normal acid was used, the residue was 6.4 per cent, the refractive index 1.5025;

with 1 part of concentrated to 1.5 parts of 38 normal acid, the residue was 7.6 per cent, the refractive index 1.5000; while with ordinary concentrated acid the residue was 13.6 per cent and the refractive index 1.4980. The effect of ordinary concentrated sulphuric acid on a pure turpentine is also shown in the following table; 38 normal acid left 0.8 per cent of viscous residue having a refractive index of 1.500.

TABLE IV.—*Effect of ordinary concentrated acid on pure turpentine.*

Procedure.	Volume of acid.	Residue.		
		Amount.	Refractive index.	Consistency and color.
	cc	Per cent.		
24 hours at 25°–30° C.....	20	12.0	1.5021	Slightly viscous, golden.
		12.0	1.5010	
24 hours at 60°–65° C.....	20	5.6	1.5200	Very viscous and dark.
		5.2		
Do.....	20	8.8	1.5184	Viscous, dark.
		8.8	1.5180	
1 hour at 95°–98° C.....	30	11.2	1.5088	Viscous.
Do.....	50	8.0	1.5130	Do.

These results indicate that the residues from the action of ordinary concentrated acid for a considerable time are not negligible, even though the volume of acid used is doubled and the temperature raised to 95° to 98° C. It is impracticable to work at this high temperature, as even with the ordinary acid there is great danger of loss from spurting or foaming. It will be observed that in all cases the residue, irrespective of its volume, is viscous and colored while its refractive index is higher than 1.500.

The effect of acids of slightly different concentration was next tried on different samples of pure spirits and on samples containing various percentages of different mineral oils. In this work 5 cc of the sample was treated with 20 cc of acid at 65° C. The results are given in Table V.

TABLE V.—*Effect of acid of several concentrations on pure and adulterated turpentines.*

Strength of acid and per cent of mineral oils present.	Residue.	Refractive index of residue at 20° C.	Consistency of residue.
	Per cent.		
38 N. ACID:			
2.5 (L. P. 8047).....	1.4	1.4910	Clear and limpid.
5 (L. P. 8047).....	2.4	1.4700	Do.
10 (L. P. 8047).....	5.0	1.4705	Do.
20 (L. P. 8047).....	12.0	1.4642	Do.
2.5 (L. P. 6377).....	1.2	1.4830	Do.
5 (L. P. 6377).....	1.8	1.4625	Do.
10 (L. P. 6377).....	4.4	1.4475	Do.
20 (L. P. 6377).....	11.0	1.4342	Do.
2.5 (L. P. 8048).....	1.0	1.4950	Do.
5 (L. P. 8048).....	1.6	1.4901	Do.
10 (L. P. 8048).....	2.0	1.4651	Do.
20 (L. P. 8048).....	8.6	1.4525	Do.

TABLE V. — *Effect of acid of several concentrations on pure and adulterated turpentines—*
(Continued.)

Strength of acid and per cent of mineral oils present.	Residue.	Refractive index of residue at 20° C.	Consistency of residue.
38 N. ACID—continued.	<i>Per cent.</i>		
2.5 (L. P. 8046).....	1.2	1.4910	Slightly oily.
5 (L. P. 8046).....	2.0	1.4822	Clear and limpid.
10 (L. P. 8046).....	4.6	1.4650	Do.
20 (L. P. 8046).....	11.2	1.4490	Do.
2.5 (naphtha).....	1.0	1.4943	Slightly oily.
5 (naphtha).....	2.0	1.4752	Clear and limpid.
10 (naphtha).....	4.6	1.4600	Do.
20 (naphtha).....	11.2	1.4259	Do.
2.5 (kerosene).....	1.8	1.4730	Do.
5 (kerosene).....	4.0	1.4640	Do.
10 (kerosene).....	7.8	1.4510	Do.
20 (kerosene).....	13.2	1.4410	Do.
2.5 (terebentine).....	.8	1.4951	Do.
5 (terebentine).....	2.0	1.4812	Do.
10 (terebentine).....			
20 (terebentine).....	11.2	1.4510	Do.
Turpentine (L. P. 1179).....	.4	1.5150	Viscous.
Turpentine (L. P. 11086).....	.4	1.5128	Do.
Turpentine (L. P. 11085).....	.6	1.5128	Do.
Turpentine.....	.4	1.5120	Do.
37.9 N. ACID:			
2.5 (L. P. 8047).....	1.6	1.4940	Clear and limpid.
5 (L. P. 8047).....	2.8	1.4805	Do.
10 (L. P. 8047).....	5.4	1.4717	Do.
20 (L. P. 8047).....	11.6	1.4633	Do.
2.5 (L. P. 6377).....	2.0	1.4830	Do.
5 (L. P. 6377).....	3.4	1.4680	Do.
10 (L. P. 6377).....	6.0	1.4435	Do.
2.5 (L. P. 8048).....	1.6	1.4960	Do.
5 (L. P. 8048).....	2.4	1.4760	Do.
10 (L. P. 8048).....	5.6	1.4580	Do.
20 (L. P. 8048).....	11.0	1.4495	Do.
2.5 (L. P. 8046).....	7.6	1.4990	Do.
5 (L. P. 8046).....	2.8	1.4800	Do.
10 (L. P. 8046).....	6.0		Do.
2.5 (kerosene).....	2.4	1.4755	Do.
5 (kerosene).....	4.4	1.4648	Do.
20 (kerosene).....	15.4	1.4390	Do.
2.5 (terebentine).....	1.4	1.4980	Do.
5 (terebentine).....	2.8	1.4785	Do.
10 (terebentine).....	5.8	1.4600	Do.
Turpentine (L. P. 1179).....	.8	1.5119	Viscous.
Turpentine (L. P. 11086).....	1.0	1.5140	Do.
Turpentine (L. P. 11085).....	.8	1.5120	Do.
Turpentine.....	1.0	1.5150	Do.
37.7 N. ACID:			
2.5 (L. P. 8047).....	2.8		
2.5 (L. P. 8046).....	2.0		
2.5 (L. P. 8048).....	2.6		
2.5 (kerosene).....	2.8		
2.5 (terebentine).....	2.6		
2.5 (NU turp.).....	2.8		
2.5 (naphtha).....	3.0		
Pure gum spirits.....	1.6		
37.6 N. ACID:			
2.5 (L. P. 8046).....	2.8		
2.5 (L. P. 8047).....	3.2		
2.5 (L. P. 8048).....	3.6		
2.5 (kerosene).....	4.0		
2.5 (terebentine).....	3.8		
2.5 (NU turp.).....	3.6		
2.5 (naphtha).....	3.6		
Pure gum spirits.....	2.2		

These figures show that a difference of 0.1 normal in the concentration of the acid makes a difference in the residue obtained, that from the 37.9 normal acid being slightly greater than the residue from the 38 normal acid. The residues from 37.7 normal and from 37.6 normal are much larger than from the 38 normal acid. The sum of the residues from mineral oil and turpentine is as great or greater than the quantity of mineral oil which was added, 2.5 per cent in these cases. It will be seen, however, that the refractive index of pure turpentine with 37.9 normal acid is practically identical with that of the residue from the 38 normal acid, and there is no difference in the consistency of the residue. In all cases the limpidity of the residue is clearly indicative of the presence of mineral oil. In no case is there any room for doubt when mineral oil is present.

DETECTION OF 1 PER CENT OF MINERAL OIL.

The high boiling fractions or distillation residues of pure turpentines leave, as a rule, no residues when treated with the 38 normal acid. The reaction between the acid and such fractions is very rapid and often violent; in some cases the material immediately becomes charcoal. This, together with the fact that on distillation of a turpentine adulterated with mineral oil there is usually a concentration of the latter in the distillation residues, makes it possible to detect or confirm the presence of mineral oil in quantities too small for positive detection in the original sample. The results showing this are given in Table VI:

TABLE VI.—Results obtained with 38 normal acid on turpentines containing small amounts of mineral oil, and on fractions of the same.

Description of sample.	Residue from original sample.			Residue from first fraction.			Residue from distillation residue.		
	Volume.	Refractive index.	Consistency.	Volume.	Refractive index.	Consistency.	Volume.	Refractive index.	Consistency.
Commercial samples:	<i>Perct.</i>			<i>Perct.</i>			<i>Perct.</i>		
1.....	3.8	1.4576		2.4	1.4750		17.6	1.4450	
2.....	1.4	1.4900	Clear and oily.	.8	1.5020	Oily.....	11.2	1.4460	Clear and limpid.
3.....	.8	1.4975	Oily.....				4.2	1.4610	Do.
Known samples: ¹									
A.....	1.2	1.5020	do.....	1.0	1.5108	Viscous.	9.0	1.4580	Do.
B.....	1.2	1.5050	Clear and oily.	1.0	1.5120	do.....	3.8	1.4570	Do.
C.....							1.6	1.4800	Do.

¹ Contained 1 per cent of mineral oil.

The sample marked "A" in Table VI was a turpentine adulterated with 1 per cent of mineral oil No. 8047. The residue from the pure turpentine with 38 normal acid was 0.8 per cent and the refractive

index of this residue was 1.5100. The refractive index of the pure turpentine was 1.4680, and of the turpentine after adulteration with 1 per cent of mineral oil, 1.4680; of the first portion distilled it was 1.4663, and of the residue from distillation, 1.4885.

Sample "B" was a turpentine adulterated in the laboratory with 1 per cent of mineral oil No. 8048 which had a specific gravity of 0.8175 and a refractive index of 1.4462; 200 cc were distilled at a pressure of 5 cm, with the results given in Table VI. The residue from distillation was 50 cc.

Sample C was made from a pure turpentine by adulterating it with 1 per cent mineral oil No. 8048; 200 cc of this adulterated sample were distilled at 5 cm pressure until 150 cc had passed over, when 5 of the 50 cc remaining were treated with 38 normal acid in the usual way.

All of these figures in Table VI show quite strikingly that the adulterants usually employed are markedly concentrated in the distillation residue; that is, in that portion of the sample which does not distill below 170° or 175° C.

The first fractions apparently are purer than the adulterated sample. The volume of the residue and its consistency and refractive index agree more nearly with those of pure turpentine than do the same constants of the original adulterated sample.

ROSIN SPIRITS.

The only substance apt to occur in turpentine that might be confounded with mineral oil is rosin spirits, which leaves a small residue, usually less than 10 per cent, similar to that left by mineral oil when treated with strong acid. A number of samples of rosin spirits of known purity were treated in the usual way with 38 normal acid, with the results given in Table VII.

TABLE VII.—*Results of action of 38 normal acid on rosin spirits.*

Substance.	Residue.		
	Per cent.	Refractive index.	Consistency.
No. 1, Rosin spirits, fraction 1.....	5.6	1.4660	Clear and limpid.
No. 2, From sodium resinate, fraction 1.....	5.6	1.4654	Do.
No. 3, Crude rosin spirits.....	1.4	1.4970	Clear and oily.
No. 4, Redistilled rosin spirits.....	6.8	1.4450	Clear and limpid.

Of No. 2, 75 cc were distilled at atmospheric pressure. The first 5 cc passing over, as well as the last 5 cc remaining in the distillation flask, were treated in the usual way. The former gave a residue of 7.8 per cent, with a refractive index of 1.4320, and was clear and limpid. The latter left a residue of 0.8 per cent, with a refractive

index of 1.5082, and was clear and oily; 30 cc of No. 1 in Table VII were distilled similarly, and when 75 per cent had passed over, 5 cc of the remaining oil were treated with acid. This gave a residue of 2.8 per cent, with a refractive index of 1.4930, and had an oily consistency.

From these results it appears that ordinary rosin spirits leaves a residue after treatment with 38 normal acid of from 2 to 6 per cent, and the refractive index of this residue agrees quite well with that of the residues from mineral oil. It appears further, that the lighter portions of rosin spirits contain the constituents which are not acted upon by the acid. This fact helps to differentiate rosin spirits from mineral oil, as the mineral oil now used in adulterating turpentine appears to be concentrated in the heavier fractions, while in the case of rosin spirits it is concentrated in the first or in the lighter fractions. As a matter of fact, however, there is little danger of mistaking rosin spirits for mineral oil, as a large percentage would have to be present to leave an appreciable residue, and when this is the case it can be distinguished by other means.

MIXING TURPENTINE AND ACID.

The importance of thoroughly mixing the turpentine with the acid has been repeatedly emphasized. This is rendered necessary by the separation of the unacted upon turpentine from the acid when the mixture is left at rest. To permit the acid to attack the globules of turpentine it is therefore absolutely necessary to mix the two repeatedly and thoroughly. To do this satisfactorily and to insure complete action, the flask should be well shaken at intervals for a total time of at least one minute during the five minutes it is being heated at 65° C. The effect of mixing is shown in the following table; 20 cc of 38 normal acid was used and the flask shaken for 10 seconds each time at 1-minute intervals:

TABLE VIII.—*Effect of mixing on character of residues.*

Method of mixing.	Residue.		
	Per cent.	Refractive index.	Consistency and color
Shaken once 10 seconds	1.6	1.4990	Slightly viscous.
	1.6	1.4993	
	1.0	1.5120	
Shaken 3 times 10 seconds each	1.0	1.5122	Viscous.
	1.2	1.5100	
	1.2	1.5100	
Shaken 6 times 10 seconds each	1.0	1.5120	Do.
	1.0	1.5125	
	0.8	1.5122	
Shaken 6 times 20 seconds each	0.8	1.5122	Do.
	0.8	1.5129	
	0.8	1.5127	
Shaken 6 times 30 seconds each	0.8	1.5127	Do.

These figures show that even with 38 normal acid it is necessary to mix thoroughly to insure that a pure turpentine is not erroneously reported to be adulterated. When the flask was shaken but 10 seconds at 65° C. the residue was 1.6 per cent, its refractive index was 1.4990, and the consistency slightly viscous or oily. If due attention were not paid to the refractive index and the consistency of the residue, this sample would be considered adulterated with from 3 to 5 per cent of mineral oil. These figures, as well as general experience, show that the flask should be shaken vigorously at 65° C. for at least one minute to insure complete conversion of the turpentine. The shaking should not be continuous but performed at intervals. It may be stated incidentally that our experience indicates that shaking for one minute will not insure the sulphonation of all the coal-tar oils in samples containing considerable quantities of these.

CONCLUSIONS.

Summarizing the preceding data, the following facts are established:

1. With a comparatively weak acid the volume of the polymerization residue from pure turpentine is variable, but with acid of the proper concentration the volume of the residue becomes practically a constant and negligible quantity.

2. The action of sulphuric acid on both pure turpentine and mineral oil is increased with rise in temperature, though to a greater extent with turpentine than with petroleum oil.

3. The relative volume of acid to turpentine is of great importance, the residue rapidly diminishing with increasing proportions of sulphuric acid.

4. The speed of conversion of turpentine is chiefly controlled by thorough mixing of turpentine and acid, the concentration of the acid, and the temperature of the reacting mixture.

5. When pure mineral oils are treated with sulphuric acid of varying concentration, from 2 to 20 or from 27 to 35 per cent of the oil is destroyed, depending on the kind of oil and the strength of the acid; also, the refractive index of the residue is lower than that of the original material.

6. When pure turpentine containing a known amount of mineral oil is treated with acid of various strengths, the following results are obtained: 38 normal acid gives a residue of from 32 to 72 per cent of the mineral oil added, when the quantity of adulterant is small (i. e., 2.5 per cent), and a residue from 43 to 76 per cent for a 20 per cent adulteration; with 37.9 normal acid a residue of from 56 to 96 per cent is obtained for low and from 55 to 77 per cent for high adulterations; with 37.7 normal acid from 80 to 120 per cent and with 37.6 normal acid from 112 to 160 per cent of residue on the basis of the oil

added, with adulterations of 2.5 per cent. With pure turpentine the 37.9 normal acid leaves a residue of 1 per cent or less; with 37.7 normal acid, 1.6 per cent; and with 37.6, 2.2 per cent.

7. The residues from pure turpentine are viscous and have a refractive index of 1.5100 or higher, while those from adulterated turpentine vary from an oily to a limpid consistency and have a refractive index of from 1.4250 to 1.5000, depending on the kind and amount of adulterant used.

8. Treating the acid with mineral oil for the purpose of saturating it and thereby minimizing its action on petroleum has no effect other than that observed when a weak acid is used; i. e., its action on turpentine and mineral oil is alike reduced.

9. As little as 2.5 per cent of mineral oil in turpentine can be detected with certainty by this modification.

10. Owing to the concentration of mineral oil in the residue when an adulterated sample is distilled and the fact that the distillation residue of a pure turpentine is completely decomposed by acid treatment, smaller quantities of an adulterant (1 or 2 per cent) may be detected with certainty by submitting the distillation residue to the action of the acid.

11. Rosin spirits in turpentine may be confounded with mineral oil unless the sample is first distilled and the residue submitted to the action of the acid. This should yield less residue if rosin spirits was employed as an adulterant and a residue greater than is left by the original material if mineral oil was used.

From the foregoing work it is evident that in order to obtain comparable and reliable results, the acid must be of a *definite, carefully determined concentration, the ratio of acid to turpentine be practically constant, the reaction always conducted at the same temperature, and the mixing of the acid and turpentine be thorough*. The primary advantage of the modification lies in the certain and rapid conversion of turpentine, leaving a negligible colored viscous residue with a refractive index greater than 1.5100.

PREPARATION OF 38 NORMAL ACID.

The sulphuric acid is prepared by adding fuming acid to the concentrated until a fuming mixture is obtained. The exact strength is then determined by diluting and titrating from 6 to 8 grams, using methyl orange as indicator. The acid is conveniently weighed in a bulb, having a capillary tube in the lower end and a tube with stopcock in the upper end, fitted with a platinum wire for weighing. The bulb is filled by aid of a slight vacuum, and the lower end of the capillary is emptied by closing the stopcock simultaneously with the withdrawal of the capillary from the acid; it may be cleaned on the

exterior by wiping first with a wet and then with a dry piece of cloth. The pipette thus filled and dried may be left for hours without losing or gaining weight.

After weighing dip the capillary into about 500 cc of water in a large beaker, open the stopcock, and when the acid has run out wash the pipette with water run in from the top through a rubber tube and funnel. Add a slight excess of sodium-carbonate solution of known strength by weight (0.2 gram per gram of solution is convenient); this may be run in from a suitably arranged dropping or delivery flask (weighed before and after the operation) until the solution is slightly alkaline to methyl orange. Boil off the carbon dioxide, allow to cool, add methyl orange, and titrate back the excess carbonate with half normal sulphuric acid.

Owing to the large amount of sulphate present, the end point is not very sharp. Some half normal alkali is, therefore, run in and the solution again made neutral. By taking the mean of several such end points a very accurate determination of the acid strength may be made. Determine the specific gravity of the acid with a pycnometer, calculate its normality, and run in from a burette having a long capillary delivery tube enough water to dilute it to 37.9 or 38 normal.

Other procedures may suggest themselves, but this method of standardization was found to be very accurate and as expeditious as any, ordinary care holding the error below 0.1 per cent.

MAINTAINING THE ACID CONCENTRATION.

It is needless to say that the acid must be carefully guarded from absorbing moisture from the air. It should be kept in one-half liter glass-stoppered bottles or stored in a reservoir bottle fitted with a 20 cc pipette, as shown in figure 1.

With the three-way stopcocks A and B in the position shown acid is siphoned into P, the displaced air passing into R. To empty the

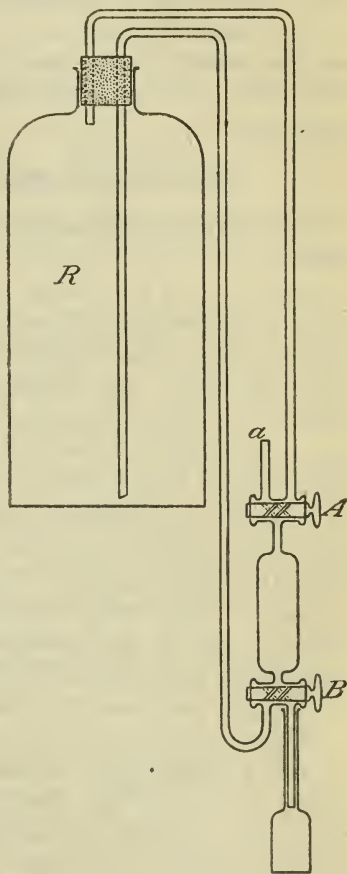


FIG. 1.—Reservoir bottle for storing acid.

pipette, A and B are turned to the position shown by the broken lines, air passing in at *a*. The acid adhering to the walls of the pipette dries this air so that when it passes into R on again filling the pipette there is no accumulation of moisture in the acid remaining in the reservoir.

The necessity for some such arrangement is shown by the following test: The polymerization residue of a pure turpentine and of one with 2.5 per cent of kerosene was 0.8 per cent and 2 per cent, respectively, using 37.8 normal acid from a 400 cc glass-stoppered bottle not previously opened, and 2.2 per cent and 3.6 per cent, using the last of the acid in the bottle which had been opened often in the meantime?

METHOD FOR MINERAL OILS IN TURPENTINE.

The details of the method as finally adopted for turpentine are as follows:

Run 20 cc of 38 normal acid into a Babcock bottle, stopper, and place in ice water, cool, add 5 cc of the turpentine, again cool, and gradually mix the contents, cooling from time to time (the temperature should not be allowed to rise materially), and when the mixture no longer warms up after shaking agitate thoroughly. Then place the bottle in a water bath in which the water is on a level with the acid and heat to from 60° to 65° C. (140° to 149° F.) in the course of from 5 to 10 minutes, keeping the contents thoroughly mixed by vigorously shaking six or seven times. Do not stopper the bottles after turpentine has been added, as they may explode.

Cool to room temperature, add ordinary sulphuric acid until the contents rise in the graduated portion of neck, and whirl at 1,200 revolutions per minute for three or four minutes, or allow to stand over night, and read the amount of supernatant liquid.

When a small amount of adulterant has been added, it is preferable to use a centrifugal machine, reading the refractive index of the upper portion of the residue immediately, as the mineral oil and residual turpentine alteration product are thus stratified, the low-reading mineral oil constituting the upper portion. A capillary pipette is used in transferring a small portion of the residual oil to the refractometer.

As the destruction of the turpentine depends upon its contact with the sulphuric acid, which in turn is dependent upon the minuteness of the turpentine particles suspended in the acid, it follows, and this is convincingly borne out by experience, that thorough mixing is one of the essential features of the method.

With a pure turpentine there will be from 0.02 to 0.05 cc of a straw-colored, viscous residue, which, if read at once, gives a refractive

index at 20° C. of 1.5100 or higher. When adulterated with mineral oil, the residue is a limpid or oily, colorless liquid, having a refractive index of 1.505 to 1.4300 or lower, depending on the kind and amount of adulterant present.

The procedure as outlined has been in use in this laboratory in connection with the food and drug work, especially, for the past four years, and in no instance when the method has been properly handled has it failed to give positive and reliable information as to the presence of mineral oil.

The volume of the residue, together with its refractive index, color, and consistency, is absolutely controlled by strict adherence to these directions and the conclusions drawn in this paper on these points are based on the stated procedure. Variations in procedure will cause variations in results, to which the conclusions given here are not strictly applicable. It is probable that other combinations of these factors can be worked out to give accurate and reliable results, but this has not yet been done.

The concentration of the acid, which, as has been stated, is very liable to change, is most conveniently determined from time to time by running a check analysis on a pure turpentine. If the residue is 1 per cent or less, with a refractive index of at least 1.5100, the acid is of the proper concentration.

This method, or modifications of it, is of course applicable to the detection of the presence of mineral oils in vegetable or in coal-tar oils. Naturally those oils, which do not react as violently with acid as terpenes do, may be heated to a higher temperature without danger of loss. Those oils which react or dissolve in acid without material increase in temperature, as the coal-tar oils do, may be handled with weaker acids. Thus the ordinary concentrated acid, quite generally used with coal-tar oils, destroys less mineral oil than does a more concentrated acid.

It may be said in conclusion that the presence in turpentine of more than about 15 per cent of mineral oil can be detected by the odor, spot test on white paper, and the presence of bubbles or "bead" on the oil when it is shaken. These are tests that the most inexperienced can apply, and it is only in those instances where the amount of mineral oil is small that resort need be had to chemical methods.

Approved:

JAMES WILSON,

Secretary of Agriculture.

WASHINGTON, D. C., November 23, 1911

